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Models for Predicting the Fate of Synthetic Chemicals in Aquatic Ecosystems

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16. ABSTRACT

The toxic effects of synthetic chemicals released into natural environments are a function of concentrations, of physico-chemical speciation, and of transformation products whose genesis is mediated by properties of the environment itself. Accurate evaluation of the probable consequences of particular releases requires an ability to forecast the speciation, transport, and transformations of chemicals. In aquatic systems, ionic and absorptive equilibria, advective and dispersive fluid transport, benthic uptake and release processes, volatilization, hydrolysis, direct and indirect photochemical processes, redox reactions, and microbial transformations have significant effects on the fate of introduced chemicals. Recent and continuing investigations of the kinetics and environmental determinants of these processes have made possible the design of models and computer codes that can generate theoretically sound forecasts of chemical events in ecosystems. These "fate codes," when coupled to equally rigorous techniques for computing effects of chemicals, can enhance the rationality, realism, and reliability of chemical safety evaluations.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

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Models for Predicting the Fate of Synthetic Chemicals in Aquatic Ecosystems

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ABSTRACT: The toxic effects of synthetic chemicals released into natural environments are a function of concentrations, of physico-chemical speciations, and of transformation products whose genesis is mediated by properties of the environment itself. Accurate evaluation of the probable consequences of particular releases requires an ability to forecast the speciation, transport, and transformations of chemicals. In aquatic systems, ionic and sorptive equilibria, advective and dispersive fluid transport, benthic uptake and release processes, volatilization, hydrolysis, direct and indirect photochemical processes, redox reactions, and microbial transformations have significant effects on the fate of introduced chemicals. Recent and continuing investigations of the kinetics and environmental determinants of these processes have made possible the design of models and computer codes that can generate theoretically sound forecasts of chemical events in ecosystems. These "fate codes," when coupled to equally rigorous techniques for computing effects of chemicals, can enhance the rationality, realism, and reliability of chemical safety evaluations.

KEY WORDS: aquatic ecosystems, mathematical models, simulation, water pollution, contaminants

The universe of synthetic chemicals is large and rapidly expanding, both in terms of production volumes and the variety of compounds available for commercial and consumer end uses. The commitment of the American people and the chemical industry to safe use and responsible handling of synthetic chemicals, as expressed in such legislative mandates as the Toxic Substances Control Act (TSCA), has significantly accelerated the growth of knowledge in ecotoxicology and environmental chemistry. Before advances in these fields can be used to enhance public safety, however, they must be coupled in a framework of realistic exposure evaluation and risk analysis.

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The toxic effects of compounds are exerted only when the compounds are released to the environment, and only insofar as sensitive organisms are exposed to deleterious concentrations for significant times. Given the rate of release or loading of a chemical on an aquatic system, the tools of environmental chemistry and ecosystem modeling and simulation can be invoked to estimate exposure, fate, and persistence of the compound. This capability is especially critical to a sensible evaluation of the risks posed by new chemicals that have not yet been released to the environment, and for evaluation of the advisability of major market expansions and new uses of chemicals already in commerce.

In this paper, the fundamental process chemistry needed for evaluation of the fate of synthetic chemicals is described, the design principles of transport and transformation computer codes expressing the consequences of the fate processes are discussed, and some sample outputs of one such code are presented. The discussion is intended as a brief introduction to chemical fate models for non-specialists. As such, its primary aim is merely to familiarize the reader with the general nature of research results and the current status of the field, and to provide an entry-level guide to the relevant literature.

Chemical Fate Processes

The "fate" of synthetic chemicals in aquatic systems encompasses two rather different concepts. First, "fate" has been used to denote the final distribution of the chemical in the system. Second, "fate" also signifies an analysis of what ultimately becomes of chemicals released into the system — that is, an answer to questions as to the percentages of the loads that are chemically transformed to secondary daughter products, volatilized, entrained in hydrologic exports, etc. The "fate processes," then, are the set of transformation and transport processes that govern the distribution and disposition of chemicals released into aquatic ecosystems.

Ionic and Sorptive Equilibria

Many synthetic chemicals are weak acids or bases, and many are very hydrophobic, having a strong tendency to leave water phases and attach or associate with solids and living things. These ionization and sorption processes can be treated, for many purposes, as being in continuous dynamic equilibrium, because the time scale of toxicological and transformation events is usually significantly slower. The set of resulting algebraic equations can be solved for the fraction of the total concentration of chemical present in each of its forms [*1*]. For example, in Fig. 1, the dissociation of hydrogen cyanide (HCN) with changing pH shows that in many ways the compound must be regarded as a composite of species with potentially very different ecotoxicological and chemical properties. Sorption of the anion is likely to be much less than that of the neutral species, volatilization will decrease as the anionic species becomes dominant, and the rates of chemical reactions of the species may be very different as well. In Fig. 2, it can be seen

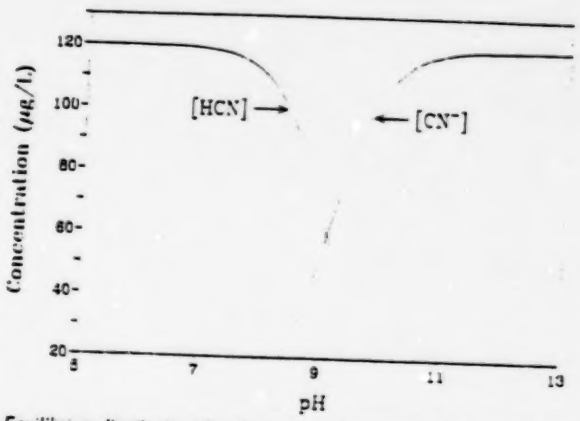

FIG. 1—*Equilibrium distribution of hydrogen cyanide between HCN and the CN^- anion as a function of pH. Total concentration 120 μg/L (from Ref 2).*

that ionic speciation also has significant toxicological consequences: the median lethal concentration (LC_{50}) falls precipitously in the vicinity of pH 9, mirroring the conversion of HCN to the CN^- anion. Thus, multivariate analyses of the biological effects of environmental factors on chemical toxicity (as illustrated in Fig. 2 for oxygen tension, temperature, alkalinity, and pH) can be interpreted only after allowance for effects of simple chemical phenomena (for example, ionization).

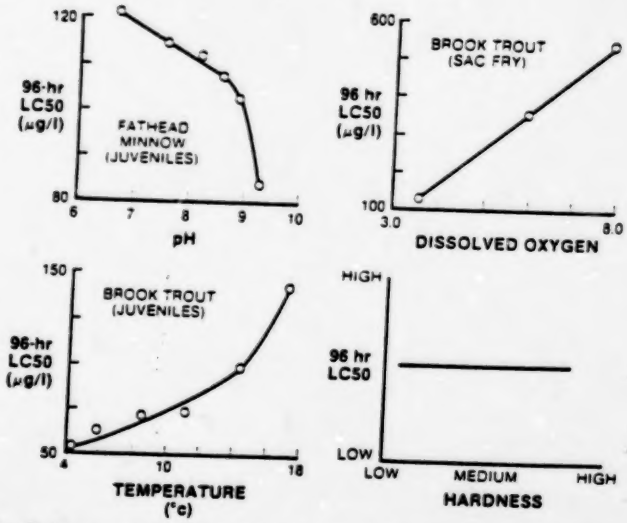

FIG. 2—*Hydrogen cyanide (HCN) 96-h LC_{50} for juvenile fishes as a function of solution pH, temperature, dissolved oxygen, and hardness* [3].

Transport Processes

Significant transport processes for synthetic chemicals include: volatilization across the air/water interface, entrainment of dissolved chemicals and chemicals sorbed with suspended sediments in hydrodynamic motions (leading to hydrologic exports and to mixing (dispersion) of the chemicals through the water body), exchanges across the benthic boundary layer, and transport in infiltrating flows and movements of the sediment bed.

Volatilization (and its converse, dissolution from the atmosphere into a water body) has been successfully modeled [*4–7*] via two-"film" or two-resistance models based on the original industrial model of Whitman [*8*]. In this approach (Fig. 3), the air/water interface is visualized as being composed of adjacent quiescent films, with turbulent, well-mixed bulk phases providing a steady renewal of material to the gradients existing in the films. The resulting mathematical description of the process allows one to compute the flux of chemical across the interface as a function of independently measurable properties of aquatic systems and of synthetic chemicals. Specifically, the mass flux is a function of the Henry's law constant (or saturation vapor pressure/aqueous solubility ratio), which measures the partitioning of the compound across the air/water interface, and of molecular velocities in the vicinity of the interface.

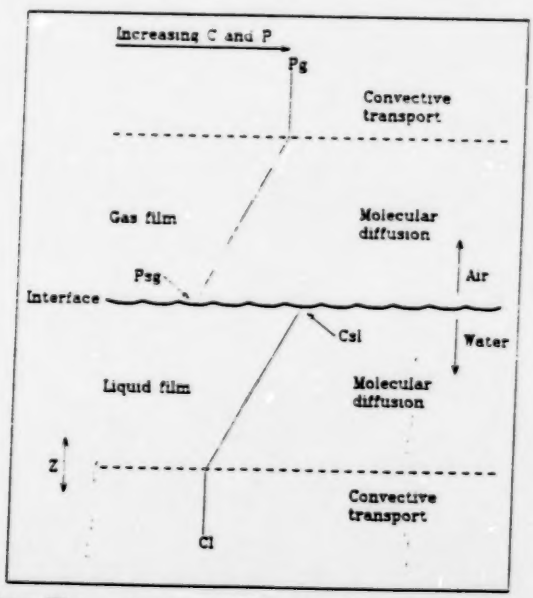

FIG. 3—*Whitman [8] two-resistance or two-film model of a gas-liquid interface: C1 is concentration (mol/m³) in bulk water. Pg is partial pressure (atm) in bulk air. Csl is aqueous concentration in liquid at the interface, and Psg is partial pressure on atmospheric side of interface (redrawn after Ref 5).*

which can be estimated from reaeration (oxygen transfer) rates and water evaporation or wind speed.

This type of model illustrates the kind of approach needed for successful chemical fate evaluations: the behavior of the chemical can be estimated without the immediate necessity of field experimentation — the chemical properties can be measured in a laboratory setting, and the environmental driving forces (the fluid and gas piston velocities) are commonly measured or inferable properties of the environment.

The interaction of synthetic chemicals with nonliving solid phases has a considerable literature [*9*], and the kinetics of sorptive processes are a subject of continuing active investigation. Still, major effects of bed sediments on the kinematics of synthetic chemicals can be deduced and described using a local equilibrium approach for sorption. In many cases, the capture of chemicals by the bed appears to result in sequestration and localization of their effects in benthic subsystems. Transfers of synthetics across the benthic boundary layer have been described using classic advection/dispersion models [*10*] or sediment transport algorithms in the currently available fate codes. This is a significant and necessary advance over earlier water quality models that ignored the bed, but may ultimately require supplementation with approaches that include an explicit treatment of kinetic factors in sorption/desorption phenomena and a more explicit and detailed treatment of biologically mediated transport processes.

Transformation Processes

Hydrolysis

The kinetics and mechanisms of chemical reactions induced by the solvent water are well known [*11–13*]. The primary reaction pathways include a neutral mechanism that is independent of pH, and specific acid- and base- (that is, $[H^+]$ and $[OH^-]$) catalyzed reactions. At constant pH, the kinetics of these transformations are "first-order" in chemical concentration, that is, the time rate of change of concentration $[C]$ is given by $d[C]/dt = -\text{Kobs}[C]$ where Kobs has dimensions of reciprocal time. (The "kinetic order" of a reaction is given by the sum of the exponents on the concentration terms in the rate expression.) The observed rate constant can be determined from the slope of the curve of the logarithm of $[C]$ versus time (Fig. 4). For chemicals subject to all three reaction pathways, the observed rate constant Kobs is a sum of the components

$$\text{Kobs} = Ka[H^+] + Kn + Kb[OH^-] \qquad (1)$$

where Ka is the acid, Kn is the neutral, and Kb is the base-catalyzed rate constant. (Note that Ka and Kb are "second-order" rate constants.) In this instance, when the logarithm of the observed rate constant is plotted against pH, a three-limb curve results as in the phenyl acetate example given in Fig. 5. For ionizable compounds, and in the presence of sorbing or complexing materials, Eq 1 must be modified to account for the speciation of the chemical. For ex-

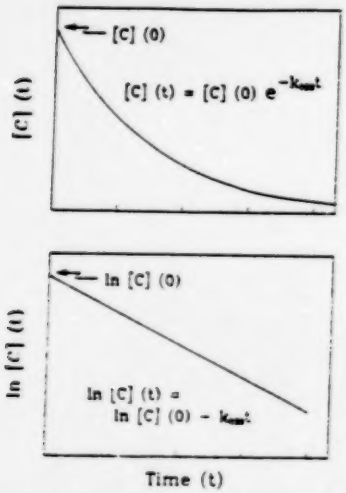

FIG. 4—*Characteristic pseudo-first-order (fixed pH) transformation curves (disappearance of parent compound) of compounds subject to hydrolysis: (upper) linear plot, (lower) semi-logarithmic plot.*

ample, in the case of the dioxane shown in Fig. 5, the neutral and base-catalyzed reactions do not occur, and the neutral and anionic species have quite different reaction rate constants. In this case, Kobs as a function of $[H^+]$ is

$$\text{Kobs} = I(0)\,(0.15)[H^+] + I(1)\,(130)[H^+] \qquad (2)$$

where the first term describes the rate of reaction of the neutral species, and the second the rate of reaction of the charged species. The term "$I(0)$" is the fraction of the total concentration present as the neutral molecule; it is simply $1/(1 + K/[H^+])$, where K is the ionization constant (the negative of whose logarithm, or pK, is 6.63). The term $I(1)$, the fraction present as the anion, is $(1 - I(0))$ or $(K/[H^+])/(1 + K/[H^+])$. Synthetic chemicals are also subject to catalysis by additional acids and bases present in natural waters (the carbonic acid system, borates, etc.). But at the concentrations typical of surface and interstitial benthic water, these reactions are generally too slow to compete with their specific acid-base counterparts [*15*].

Direct and Indirect Photochemical Reactions

Direct photochemical transformations of synthetic chemicals are a consequence of the absorption of electromagnetic energy by the chemical molecule. In this "primary" photochemical process, absorption of a photon promotes the molecule from its ground state into an electronically excited state. The excited molecule then either reacts to yield a photoproduct or decays (via fluorescence, phosphorescence, etc.) to its ground state. The efficiency of each of these energy

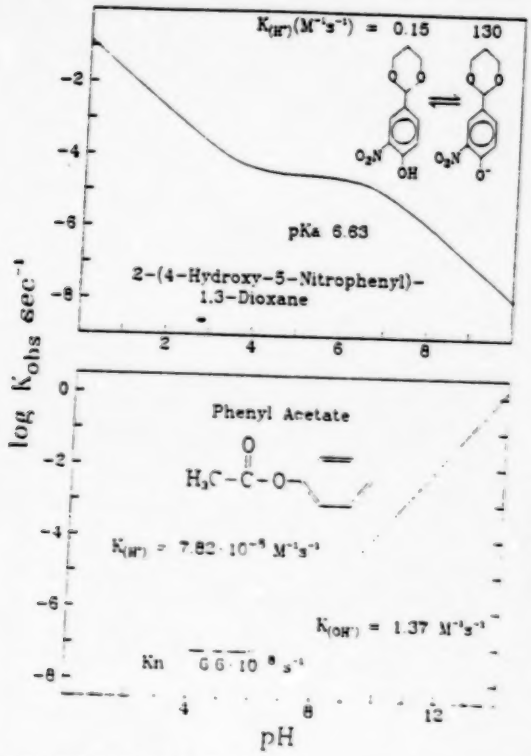

FIG. 5—(Lower) *hydrolysis pH-rate profile of phenyl acetate at 25°C, constructed from data in Ref 12.* (Upper) *hydrolysis pH-rate profile of a substituted 2-phenyl-1,3-dioxane constructed from data in Ref 14.*

conversion processes is called its "quantum yield." Photochemical reactivity thus is composed of two factors: the absorption spectrum and the quantum efficiency for photochemical transformations.

The rate of photolytic transformations in aquatic systems also depends on the intensity and spectral distribution of light in the medium [*16*]. Light intensity decreases exponentially with depth. This fact, known as the Beer-Lambert law, can be stated mathematically as:

$$d(E0)/dZ = -K(E0)$$

where

$E0$ = photon scalar irradiance (photons/m^2/s),
Z = depth (m), and
K = diffuse attenuation coefficient for irradiance ($/m$).

The product of light intensity, chemical absorptivity, and reaction quantum yield, when integrated across the solar spectrum, yields a pseudo-first-order photochemical transformation rate constant with units of reciprocal time, as for Kobs in Eq 1.

Indirect Photolysis and Oxidation

The simultaneous occurrence of "humic materials," dissolved oxygen, and sunlight often results in an acceleration of the rate of transformation of synthetic organic chemicals [*17,18*]. These reactions are termed "indirect" or "sensitized" photolysis. Indirect photolysis can be subdivided into two classes of reactions. First, "sensitized photolysis" *per se* involves excitation of a (humic) sensitizer by sunlight, followed by direct chemical interaction between the sensitizer and a synthetic compound. The second class of indirect photolysis involves the formation of chemical oxidants, primarily via the interaction of sunlight, humic materials, and dissolved oxygen [*19*]. The primary oxidants known to occur in natural waters are hydroxyl and peroxy radicals [*20*] and singlet oxygen [*21*]. Most aquatic fate codes represent the oxidative transformation of synthetic chemicals via a purely phenomenological coupling of a second-order rate constant (with units/mole/litre/time) to the concentration (moles/litre) of oxidants in the system. (The same is true of reduction reactions, or redox in general, although further research can be expected to relieve this situation in the future.) The occurrence and concentration of oxidants in natural waters have been investigated via the laboratory irradiation of solutions of test compounds that react preferentially with chemical oxidants to give distinctive products (chemical "probes") [*20–22*].

Microbial Biotransformation

Microbial population growth and substrate utilization can be described via Monod's [*23*] analogy with Michaelis-Menten enzyme kinetics [*24*]. The growth of a microbial population in an unlimiting environment is described by: $dN/dt = \mu N$, where μ is called the "specific growth rate" and N is microbial biomass or population size. The Monod equation modifies this by recognizing that consumption of resources in a finite environment must at some point curtail the rate of increase (dN/dt) of the population:

$$\mu = \mu(\max)\frac{[S]}{Ks + [S]} \tag{3}$$

in which $[S]$ is the concentration of the growth-limiting substrate, $\mu(\max)$ is the "maximum specific growth rate" attained when $[S]$ is present in excess (that is, nonlimiting), and Ks, the "saturation constant" is that value of $[S]$ allowing the population to grow at rate $\mu(\max)/2$. An equation describing the behavior of $[S]$ over time, and thus by implication the dynamics of a biodegradable synthetic

compound $[C]$, follows via a simple derivation [24], resulting in Eq 4, in which Y is the "yield coefficient" in cells or biomass produced per unit C metabolized.

$$\frac{dC}{dt} = -\frac{\mu(\max)}{Y}\frac{[C]}{Ks + [C]}N \tag{4}$$

Although useful in the context of laboratory investigations, this equation is difficult to apply in a broader ecological context. The first difficulty is mechanical: Eq 4 is nonlinear in its parameters, and thus imposes a high cost in computation time when used in a computer code. For trace concentrations (that is, $[C] \ll Ks$), however, the term $(Ks + [C])$ in Eq 4 can be approximated by Ks, giving

$$\frac{d[C]}{dt} = -\frac{\mu(\max)}{YKs}N\,[C] \tag{5}$$

This formulation is similar to the "second-order" equations used to describe the kinetics of chemical reactions (for example, Eq 1), and $\mu(\max)/(YKs)$ by analogy can be called a second-order biolysis rate constant K_{b2}, with units/time/(cells/litre) when population sizes, N, are expressed in cells or colony forming units (CFU) per litre.

There are conceptual difficulties as well, however. A natural microbial community derives its energy from a variety of sources. A species restricted to exploitation of a trace-level synthetic compound as its sole carbon source would be at a severe competitive disadvantage; estimation of the population densities of metabolically specialized biotransformers in real systems is problematic at best. Further, the presence of multiple energy-yielding substrates violates a fundamental assumption of the Monod approach, that is, that $[C]$, the synthetic compound, limits growth. Compounds may be transformed in energy-requiring detoxification processes, making the concept of cell yield (Y) of dubious utility. When the chemical is degraded without a change in population size, the zero yield invalidates Eqs 4 and 5 alike. (This phenomenon is sometimes called "cometabolism" [25].) Finally, one might expect that the transformation of trace-level compounds might constitute the exclusive province of non-opportunistic "oligotrophic" sub-populations, leading to an apparent constancy of the first-order rate constant for some compounds and an independence of rates in the face of large population variations among the opportunist "eutrophic" components of the microbial flora.

Still, the rate of transformation of synthetic organics presumably must depend on intrinsic chemical properties or the structure of the compound, and the metabolic capacity of microbial communities. The simplest expression of this duality is the second-order equation

$$d[C]/dt = -K_{b2}B[C] \tag{6}$$

which asserts that the rate of biolysis $(d[C]/dt)$ is first-order in compound concentration $[C]$ and in microbial activity B, and in which an identification of

K_{b2} with $\mu(\max)/(YKs)$ is discarded. This semi-empirical technique is used by most currently operational exposure models.

The first-order transformation of synthetic compounds at fixed population sizes, and a direct proportion of that rate constant to population size (that is, the situation expressed in Eq 6), has been observed in a number of instances [*26*] (Fig. 6). Furthermore, in some cases, the rate per cell (K_{b2}) has been observed to be independent of the growth phase of the population (Fig. 7). Despite these encouraging observations, however, considerable variance and substantial qualitative changes in biolysis rates remain to be explained (see, for example, the discussion by Lewis, Kellogg, and Holm in this volume).

Aquatic Fate Computer Codes

Given an adequate description of the dominant fate processes, it remains to organize these models into a coherent analysis system, and to generate conclusions or outputs that can be used in safety evaluations. The tools of system simulation and computer modeling developed in the context of systems ecology and pollution control engineering over the past several decades have been employed for this purpose, resulting in the creation of perhaps seven or eight

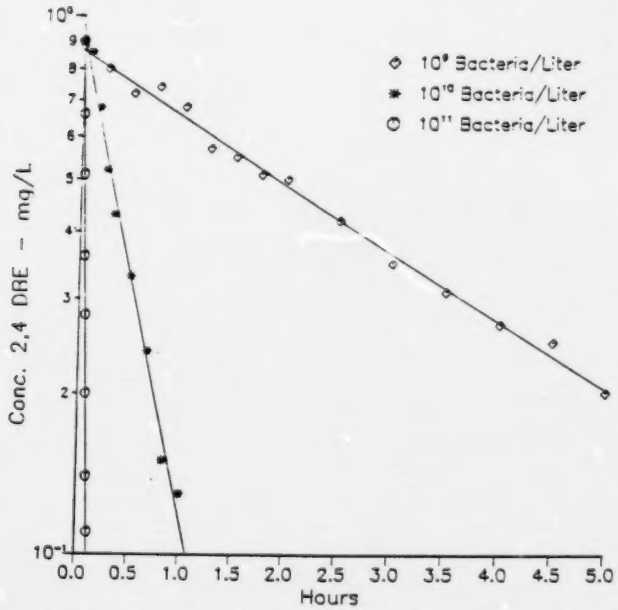

FIG. 6—*Microbial transformation kinetics of butoxyethyl ester of 2,4-dichlorophenoxyacetic acid. Bacterial populations from Overlook Lake, GA; population densities measured via 48-h incubations at 22°C on TGA agar* [26].

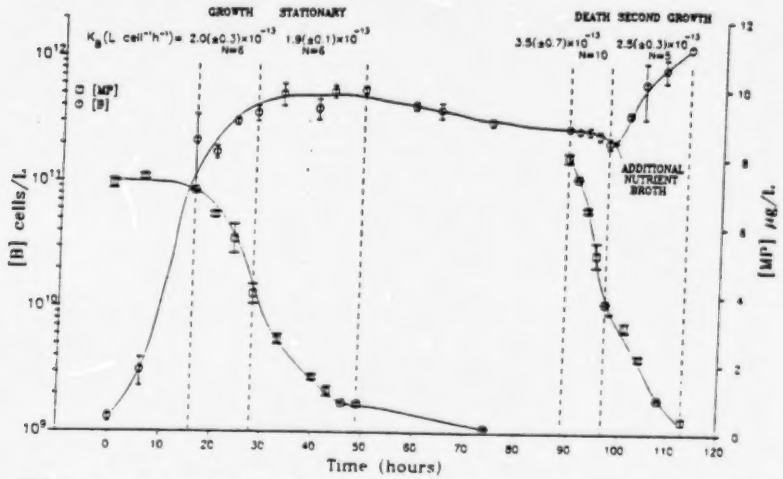

FIG. 7—*Time course of biolysis of methyl parathion by* Flavobacterium aquatile *in nutrient broth during a variety of growth phases of the experimental population. Note relative stability of the second order biolysis rate constant (*K_{B2}*, Eq 6). (Figure courtesy of D. L. Lewis.)*

finished computer codes (or code families) useful for evaluating synthetic toxic chemicals in aquatic systems [*27*].

All these codes use numerical integration of a set of differential equations to compute the fate and exposure of chemicals, given a load on the system. Conceptually, the approach involves a mass balance for a typical segment of the system (Fig. 8), in which mixing within the segment is fast enough that internal gradients in chemical concentration do not seriously affect the computations. The mass

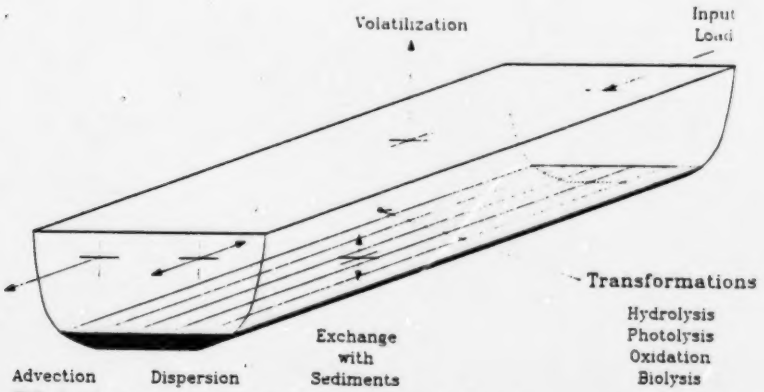

FIG. 8—*Segment of aquatic system used as a control volume for constructing a mass balance equation. The rate of change of chemical concentration in the segment is governed by the chemical loadings, transport processes, and transformation sinks for the chemical.*

balance then accounts for the change in concentration of the chemical over some time period as a function of the difference between the external loadings and dispersion from more concentrated zones (added mass), less the advected and volatilized losses, transformations, and losses (or gains) from benthic subsystems. In the finished codes, whole systems are represented as a matrix of connected segments, as for example the seven-segment lake model diagrammed in Fig. 9.

From the systems models (that is, the complete mass balance, hydrodynamic, and transport models linking the spatial segments of the water body), several kinds of outputs can be derived. For example, when the codes are driven with time-varying environmental data and projected chemical loadings, the seasonal patterns of exposures, and the frequency and severity of acute stress events on resident organisms can be computed from the concentration time-series produced by the codes. For evaluation of the general climate of chronic exposures to be expected, long-term or steady-state solutions can be invoked. Further, the fate of the compound can be partitioned among processes, thus indicating which processes are dominant and thus require the most accurate laboratory determinations of chemical properties.

For example, Figs. 10 and 11 are outputs from the EXAMS2 code [*28*], using the lake model of Fig. 9. In Fig. 10, the code output indicates that direct photolysis and biolysis in the water column are the primary transformation processes governing chemical fate, and the code produces a block of internal check data confirming that the model properly closed its mass balances. Figure 11 is the summary output from the EXAMS2 code, run in its steady-state option for chronic exposure evaluation and chemical screening studies. In this code, the

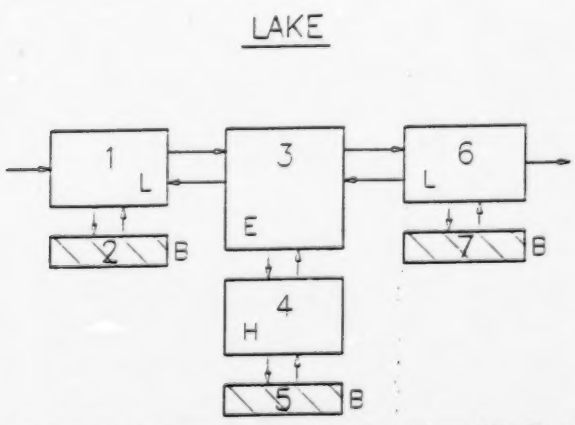

FIG. 9—*Segment model of lake used as test data for the EXAMS2 code* [28]. *The segment codes indicate littoral zones* (L), *benthic sediments* (B), *epilimnion* (E), *and hypolimnion* (H). *Dispersive mixing pathways are indicated by the pairs of arrows denoting material exchanges, and the influent and export streams are shown by the entry and exit arrows at Segments 1 and 6, respectively.*

EXAMS -- EXposure Analysis Modeling System -- V 2.7: Mode 1
Ecosystem: EUTROPHIC LAKE -- AERL CODE TEST DATA
Chemical: BENZO[f]QUINOLINE

TABLE 18.01. Analysis of steady-state fate of organic chemical.

Steady-state Values by Process	Mass Flux Kg/day	% of Load	Half-Life* Days
Hydrolysis			
Reduction			
Radical oxidation			
Direct photolysis	1.490	68.58	117.4
Singlet oxygen oxidation			
Bacterioplankton	0.5352	24.64	326.7
Benthic Bacteria	1.0448E-02	0.48	1.6735E+04
Surface Water-borne Export	0.1360	6.26	1286.
Seepage export			
Volatilization	6.3371E-04	0.03	2.7591E+05
Chemical Mass Balance:			
Sum of fluxes =	2.172		
Sum of loadings =	2.172		
Allochthonous load:		100.0	
Autochthonous load:		0.0	
Residual Accumulation =	4.54E-05	0.0	

* Pseudo-first-order estimates based on flux/resident mass.

FIG. 10—*Sample output from EXAMS2 code: analysis of transformational fate of benzo[f]quinoline in the lake diagrammed in Fig. 9.*

summary output is organized into exposure, fate, and persistence sections. The exposure section reports the maximum concentration observed in the system, the fate section reports both distributional and transformational fate of the compound, and the persistence section estimates the time required for the system to recover when the external loadings cease.

The computer codes provide a means of systematic extrapolation of the results of laboratory tests to environmental systems. The uses of the codes include an analysis of critical data needs, determination of the toxicological consequences from the expected exposure concentrations, and evaluation of the tendency of compounds to persist in the environment. The codes themselves require validation, a process that includes a thorough examination of the accuracy with which the underlying science and mathematics have been mechanized, evaluation of the impact of the assumptions and simplifications used to construct the process models, and comparison of the outputs from the codes with observational data [*29*]. Thorough evaluation of fate codes has been hampered by a paucity of adequate data sets. Deficiencies in the descriptive data surrounding a test case introduce free parameters into the codes' input data bases, which in turn rapidly degrades the "validation" to a curve-fitting exercise of limited value. The validity of the codes depends on the validity of the underlying process models; the latter are the subject of specific research efforts and distinct literatures [*30*]. A detailed discussion of the validation problem in the context of chemical fate codes can be found in Ref. *29*, and some specific validation studies can be found in Refs. *31*, *32*, and *33*.

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   EXAMS -- EXposure Analysis Modeling System -- V 2.7: Mode 1
Ecosystem: EUTROPHIC LAKE -- AERL CODE TEST DATA
Chemical: BENZO[f]QUINOLINE
------------------------------------------------------------------
TABLE 20.01.  Exposure analysis summary.
------------------------------------------------------------------
Exposure (maximum steady-state concentrations):
 Water column: 1.260E-02 mg/L dissolved; total = 1.292E-02 mg/L.
 Benthic sediments: 1.147E-02 mg/L dissolved in pore water;
   maximum total concentration =  14.4      mg/kg (dry weight).
 Biota (ug/g dry weight): Plankton =  6.1      Benthos =  5.5

Fate:
 Total steady-state accumulation:  252.      kg, with  15.58%
   in the water column and 84.42% in the benthic sediments.
 Total chemical load:  2.2      kg/day.  Disposition:  68.58%
   chemically transformed,  25.12% biotransformed,  0.03%
   volatilized, and  6.26% exported via other pathways.

Persistence:
 After  156.      days of recovery time, the water column had
   lost  67.48% of its initial chemical burden; the benthic zone
   had lost  42.03%; system-wide total loss of chemical =  46.0%.
 Five half-lives (>95% cleanup) thus require about     30. months.
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FIG. 11—*Sample output summary from EXAMS2 code: benzo[f]quinoline in example lake (Fig. 9).*

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